# Critical behavior of the liquid gas transition of 4 He confined in a silica aerogel

Geoffroy Aubry, Fabien Bonnet, Mathieu Melich, Laurent Guyon, Florence Despetis, Pierre-Etienne Wolf

**Journal of Low Temperature Physics manuscript No.**
(will be inserted by the editor)

**G.J. Aubry**[1] · **F. Bonnet**[1] · **M. Melich**[1] ·
**L. Guyon**[1] · **F. Despetis**[2] · **P. E. Wolf**[1]

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11.07.2012

**Keywords** phase transition · confined systems · critical behavior · light scattering · RFIM

**Abstract** We have studied $^4$He confined in a 95% porosity silica aerogel in the vicinity of the bulk liquid gas critical point. Both thermodynamic measurements and light scattering experiments were performed to probe the effect of a quenched disorder on the liquid gas transition, in relation with the Random Field Ising Model (RFIM). We find that the hysteresis between condensation and evaporation present at lower temperatures disappears at a temperature $T_{ch}$ between 25 and 30 mK below the critical point. Slow relaxations are observed for temperatures slightly below $T_{ch}$, indicating that some energy barriers, but not all, can be overcome. Above $T_{ch}$, no density step is observed along the (reversible) isotherms, showing that the critical behavior of the equilibrium phase transition in presence of disorder, if it exists, is shifted to smaller temperatures, where it cannot be observed due to the impossibility to reach equilibrium. Above $T_{ch}$, light scattering exhibits a weak maximum close to the pressure where the isotherm slope is maximal. This behavior can be accounted for by a simple model incorporating the compression of $^4$He close to the silica strands.

PACS numbers: 67.25.dr, 05.70.Jk, 64.60.My, 68.03.Fg

## 1 Introduction

Despite intense theoretical and experimental efforts, the effect of quenched disorder on phase transitions remains not fully understood. While this question has originally arisen in the context of magnetism, it has been extended to fluids confined in disordered porous materials, in particular tenuous silica gels or aerogels which offer an unique experimental realization of a self-sustained, dilute,

1: Institut Néel CNRS-UJF, BP 166, F-38042 Grenoble CEDEX 9, France
E-mail: pierre-etienne.wolf@grenoble.cnrs.fr
2: Lab Charles Coulomb UMR 5221 CNRS-UM2, F-34095 Montpellier CEDEX 5, France

quenched disorder. Focusing on the Ising universality class, Brochard and de Gennes have suggested that the demixtion of a binary liquid confined in a gel should be an experimental realization of the Random Field Ising Model (RFIM) and of its critical behavior[1], at least close enough to the bulk critical temperature $T_c$ for the fluid correlation length to be larger than the gel correlation length. In the same spirit, a number of studies have concerned the liquid-gas transition of $^4$He confined in aerogels. Early experiments by Wong and Chan[2] have been interpreted in terms of a genuine first-order equilibrium phase transition existing in a *wide* temperature range, with a shifted critical point and a modified critical exponent for the order parameter (the density difference between liquid and gas), due to the disorder. However, latter experiments on $^4$He in aerogels[3,4,5,6] have revealed a strong hysteresis between condensation and evaporation, persisting up to close to the critical temperature[5] , indicating that the system cannot reach equilibrium. A remarkable feature is that, at low temperatures or large porosities, the adsorption isotherm presents a quasi-plateau of pressure, just like for a regular first-order, equilibrium, transition[4,5,6,7]. In fact, this behavior turns out to be consistent[6] with the prediction originally made for the zero temperature RFIM[8], and generalized to the case of the liquid-gas transition at finite temperature[9,10,11], of a disorder-driven, non equilibrium, phase transition, where condensation occurs by athermal avalanches, whose size diverges below a critical temperature (or disorder).

These results leave open the possibility that, very close to $T_c$, the energy barriers for condensation become small enough for the system to be described by the equilibrium RFIM, characterized by a true phase transition below a critical temperature $T_c^*$, and non bulk critical exponents at $T_c^*$[12]. Experiments on $N_2$[13] and isobutyric acid-water[14] confined in (aero)gels have been interpreted as showing such an equilibrium behavior, while the observation of slow dynamics above $T_c^*$ in these experiments fitted with the initial theoretical suggestion that, above $T_c^*$, the Ising RFIM model could present an equilibrium glassy phase[15]. However, it has been recently rigorously shown that only an out of equilibrium glassy phase is possible[16] above $T_c^*$, and it is not clear how the experiments fit this picture.

In contrast, two other experiments find no evidence for any equilibrium critical behavior. For $^4$He confined in aerogels, isotherms measurements very close to $T_c$, in the region where the hysteresis disappears, show no true pressure plateau, *i.e.* no indication of an equilibrium phase transition[5]. On the other hand, neutron scattering measurements performed on $CO_2$ confined in a silica aerogel close to the bulk critical point[17,18] show that the fluid correlation length remains finite, consistent with a suppression of the phase transition due to disorder. In this paper, we revisit this question by combining, in a single experiment, high resolution isotherms *and* light scattering measurements for $^4$He confined in aerogels close to $T_c$.

## 2 Experimental

We have studied two aerogels samples with the same porosity (95%) and different microscopic structures, obtained respectively by synthesis in basic (B102) or neutral (N102) conditions. Both samples are about 3.7 mm thick and 14 mm in diameter and located in an optical cell, allowing light scattering measurements at 45° and 135° from the incident direction[6]. The cell temperature is measured by

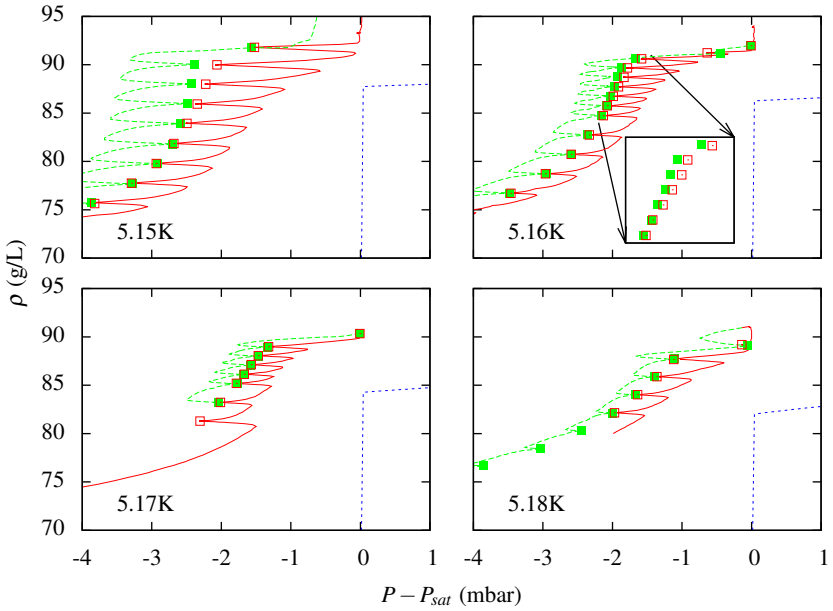


**Fig. 1** (Color online) Isotherms in B102 close to $T_c$. The solid line (red online) is the adsorption branch, while the dashed line (green online) is the desorption branch. The dashed line in the lower right corner (blue online) represents the bulk isotherm[20] for the given temperature. Bulk gas densities are out of range on the scale of this figure and fall between 52 g/L (5.15 K) and 57 g/L (5.18 K). Hysteresis closes between 5.16 K and 5.17 K.

a germanium resistor, and regulated to about 10 $\mu$K by a heater glued onto the cell walls. Condensation is controlled by changing between 80 K and 200 K the temperature of an external reservoir connected to the cell[19]. The mass condensed into the aerogel is precisely obtained from the total amount of $^4$He in the system and the reservoir temperature[6]. The pressure is measured by a room temperature sensor connected to the cell by a separate capillary. During condensation, latent heat is released and flows to the cell walls, causing a local increase of the $^4$He temperature, due to its poor thermal conductivity. In order to suppress this thermal gradient, we stop condensation at regular time intervals and let the system thermally relax about one hour while continuously measuring the pressure $P$ and the heating power $W_h$ necessary to regulate the cell temperature.

## 3 Isotherms

Figure 1 shows isotherms for B102 close to $T_c$=5.195 K, for condensation or evaporation rates between 0.25 and 0.50 $\mu$mol/s. Each stop is followed by a relaxation of the pressure. Once the pressure has relaxed, the loop remains open at 5.15 K and 5.16 K while it is closed at 5.17 K and 5.18 K within our pressure resolution (10 $\mu$bar). Hence, the hysteresis loop closes between 25 and 35 mK below $T_c$, in agreement with the results of Herman *et al.* on a similar aerogel[5]. This is in-

termediate between the temperatures (respectively 9 and 65 mK below $T_c$) where the bulk correlation length $\xi$ [21], and the interface width (3.6 $\xi$ [22]) become equal to the estimated aerogel correlation length of 10 nm [6] . For the two temperatures between the closure temperature $T_{ch}$ and $T_c$, the isotherm does not present any pressure plateau. As Herman *et al.* [5], we do dot find any evidence for any equilibrium long range order below $T_c$.

The isotherms present a kink at a certain density, above which the pressure rises faster, with a slope comparable to that of the bulk isotherms just above the saturated pressure, showing that the kink marks the end of the condensation inside the aerogel. The corresponding density of the confined liquid is only slightly larger than the bulk density (at most 10%). While this agrees with ref. [5] and the fact that most of $^4$He is far enough from the silica strands not to be compressed by the Van der Waals interaction, this contrasts with the conclusion of ref. [18], based on neutrons transmission measurements, that the average density of $CO_2$ in aerogel close to the critical point is 50% larger than in the bulk. We will come back to this point in §5.

## 4 Pressure relaxation and slow dynamics

We have searched for slow dynamics characteristic of disordered systems by examining in detail the relaxation of pressure following each condensation step. At 4.8 K, far below $T_c$, figure 2(a) shows that once the condensation is stopped, $P$ and $W_h$ relax to their final values with a similar time scale of about 5 minutes. This is comparable to the computed decay time (2 minutes) of the slowest mode of thermal diffusion in a 3.7 mm thick slab filled with bulk liquid, suggesting that the observed pressure relaxation could be related to the cooling of $^4$He following the stop of condensation. Indeed, we have checked that decreasing the cell temperature at constant filling on the pressure quasi-plateau does shift the measured pressure by the corresponding change in the saturated vapor pressure (about 1.3 mbar per mK).

Figures 2(b) and (c) show relaxations close to $T_c$, below and above $T_{ch}$. $W_h$ relaxes on the same time scale of 5 minutes with an amplitude proportional to the initial flow rate, consistent with a thermal effect similar to that at 4.8 K. In contrast, the pressure relaxes on a longer time scale, which depends on the average density and is maximal close to full condensation. We can fit the observed relaxation by a sum of two exponentials, one proportional to $W_h$ due to thermal relaxation, the other with a slower decay rate (about 8 minutes at 5.15 K and 12 minutes at 5.18 K close to full condensation) which could reflect slow dynamics of the fluid distribution inside the aerogel. This would be consistent with the existence of energy barriers. The longer relaxation time at 5.18 K could result from the fact that unsurmountable barriers below $T_{ch}$ can be overcome on the observation time scale. However, on the one hour timescale of our measurements, we do not observe the stretched exponential behavior expected for a glassy dynamics associated with a distribution of barriers. Direct measurements of the fluid dynamics using photon correlation spectroscopy would be needed to elucidate whether this feature could be due to our limited pressure resolution.

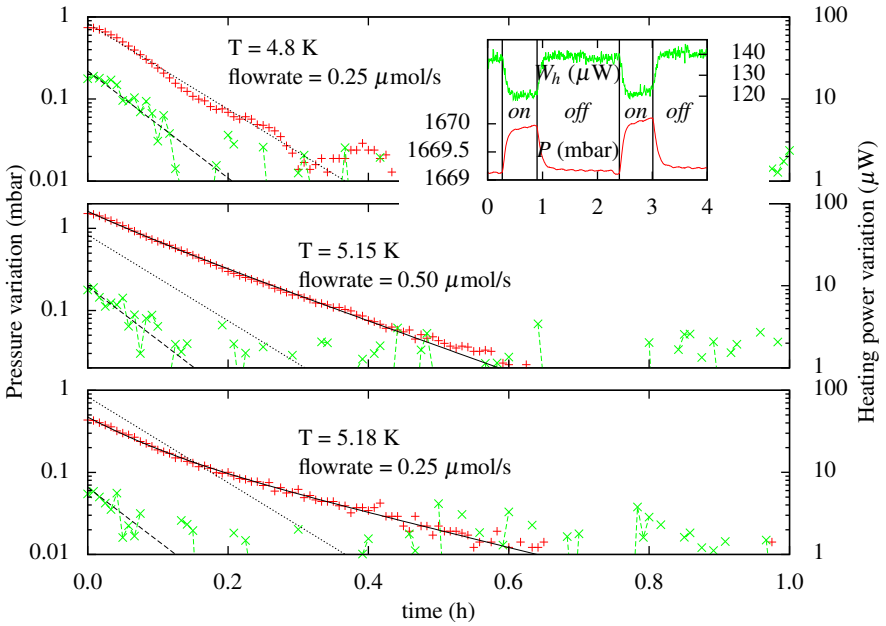


**Fig. 2** (Color online) Relaxations of the pressure $P$ (+) and of the heater power $W_h$ (×) following a condensation step at three temperatures. The inset shows $P$ and $W_h$ at 4.8 K with the flow rate *on* or *off*. The behavior at 4.8 K is fitted with single exponentials and is attributed to thermal relaxation. For 5.15 K and 5.18 K, the dashed and dotted lines are exponentials with the decay rates measured at 4.8 K for $P$ and $W_h$. Pressure relaxation of $W_h$ at 5.15 K and 5.18 K is slower than at 4.8 K and can be fitted (solid lines) by the pressure relaxation at 4.8 K, rescaled by the amplitude of $W_h$, plus a slower exponential, which we attribute to slow dynamics of the fluid distribution near $T_{ch}$.

## 5 Light scattering close to $T_c$

Figure 3(a) shows the intensity scattered at 45° as a function of pressure for B102. For $T \leq T_{ch}$, this signal (as well as that at 135°) increases in the region of the hysteresis loop. In N102, the light scattered by the entrance region of the laser sheet at 135° shows a similar behavior (the light scattered by other regions, or at 45°, is dominated by the strong silica background of N102[6]). As at lower temperatures[6], this behavior is consistent with the progressive growth of microscopic static liquid domains as the pressure increases. The decrease of the signal with temperature is consistent with the decrease in the optical contrast between liquid and gas as the bulk critical temperature is approached. In this interpretation, one could expect the optical signal to vanish at $T_c$. However, measurements in N102 performed 3 and 50 mK above $T_c$ show a continuous increase of the scattered intensity up to the region of maximal slope in the bulk pressure-density isotherm, followed by an abrupt drop to the background silica level (Figure 3(b)). Correlatively, the measured transmission drops in the region of the peak in the scattered intensity (the logarithm of the extra attenuation with respect to the bare silica being proportional to the scattered signal at 135°, as expected). While this behavior could evocate critical opalescence, it can be accounted for by the concept of critical adsorp-

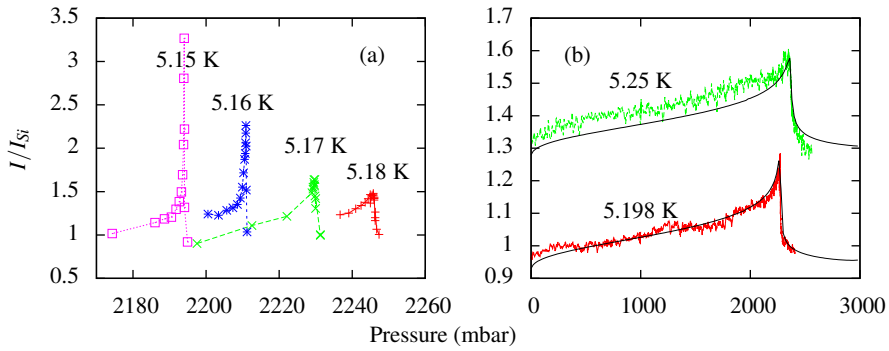


**Fig. 3** (Color online) Pressure dependence of the light intensity scattered at 45° for B102 (a) and 135° for N102 (b), normalized by the intensity $I_{Si}$ scattered by the bare aerogel. In figure (b), the curve at 5.25 K is vertically shifted by 0.3 for clarity. Figure (b) also shows the theoretical dependence of the excess mass adsorbed on a flat silica substrate, rescaled for comparison to the optical signal (see text).

tion[23]. The van der Waals attraction by the silica, combined with the large bulk compressibility of $^4$He close to $T_c$, increases the density of $^4$He close to the silica strands, hence the scattered signal, in a similar way to the case of an adsorbed film[24]. With respect to an homogeneous situation, the scattered field is increased by a quantity proportional to the excess mass with respect to the bulk, defined as the volume averaged difference between the local density and the bulk density at the external pressure. This quantity can be computed as a function of temperature in the case of a planar substrate, using the bulk state equation of $^4$He[20] and the van der Waals attraction given in ref.[25]. As shown by figure 3(b), the temperature dependence of the obtained excess mass reproduces quite well the observed scattered intensity, the scaling factor being close to that computed from the known dielectric constants of silica and $^4$He, and a typical diameter strand of 2 nm. On the other hand, the measured extra scattering due to $^4$He (about 25% of the silica contribution, corresponding to a mean free path of 10 mm) is nearly thousand times larger than the (separately measured) bulk scattering signal at $T_c$ and 45°. Here also, photon correlation spectroscopy would be needed to separate possible critical thermodynamic temporal fluctuations from the strong static contribution of critical adsorption.

Finally, we note that our results for N102 are quite similar to those obtained on $CO_2$ using neutrons rather than light scattering[18]. This suggests that, in the latter case, the decrease in transmission measured near $T_c$ close to the critical pressure is also due to the increase of scattering due to critical adsorption. Extracting the fluid density from the neutrons transmission, as the authors of ref.[18] do, would then be incorrect. This might be the origin of the reported large increase of the confined density with respect to the bulk fluid for $CO_2$ (see §3).

## 6 Conclusions

In summary, in contrast to refs.[2,13,14], our experimental results do not show any equilibrium first order transition above $T_{ch}$, the closure temperature of the hys-

teresis loop. Either, the transition predicted by the RFIM lies inside the hysteretic region below $T_{ch}$, or the temperature above which the bulk $^4$He correlation length is large enough for the RFIM to apply is larger than $T_c^*$, the critical temperature of the RFIM model. On the other hand, around $T_{ch}$, the relaxation of pressure does not show any clear clear evidence for marked glassy dynamics. Finally, close and above the bulk critical temperature, the optical signal is dominated by the static contribution resulting from the large compressibility of $^4$He, masking any possible critical dynamic contribution. To go further, we plan to improve the sensitivity of our measurements by using photon correlation spectroscopy to directly detect small dynamic changes of the fluid distribution.

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